

CONF-841184--20

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

LA-UR--84-3486

DE85 003724

TITLE $\text{UFe}_4\text{P}_{12}$ and $\text{CeFe}_4\text{P}_{12}$: Non-Metallic Isotypes of Superconducting
 $\text{LaFe}_4\text{P}_{12}$

AUTHOR(S) G. P. Meisner, M. S. Torikachvili, K. N. Yang, M. B. Maple,
and R. P. Guertin

SUBMITTED TO Annual Meeting on Magnetism and Magnetic Materials
San Diego, CA, November 27 - 30, 1984

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By acceptance of this article the publisher recognizes that the U S Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution or to allow others to do so for U S Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U S Department of Energy.

DISTRIBUTION OF THIS REPORT IS UNLIMITED

 **Los Alamos** Los Alamos National Laboratory
Los Alamos, New Mexico 87545

UFe₄P₁₂ AND CeFe₄P₁₂: NON-METALLIC ISOTYPES OF SUPERCONDUCTING LaFe₄P₁₂

G. P. Meisner^(a) Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545.

M. S. Torikachvili, K. N. Yang and M. B. Maple, Institute for Pure and Applied Physical Sciences, University of California, San Diego, La Jolla, CA 92093.

R. P. Guertin, Department of Physics, Tufts University, Medford, MA 02155.

The new compound UFe₄P₁₂, which was found to be isostructural to superconducting LaFe₄P₁₂ and with a lattice constant of 7.7729 Å, is a semiconductor and shows ferromagnetic order below 3.15 K.

CeFe₄P₁₂ is also a semiconductor and its magnetic susceptibility is unusually small in comparison to LaFe₄P₁₂. The semiconducting behaviors of both UFe₄P₁₂ and CeFe₄P₁₂ seem anomalous and may arise from strong f-electron hybridization.

72.80.Jc, 75.50.Dd, 75.30.Gr

As part of our investigation of various types of f-electron materials, we have included the study of a system of ternary iron phosphide compounds with the general formula MFe_4P_{12} , where M can be the elements La through Eu⁽¹⁾, Th⁽²⁾ or U. The compound $LaFe_4P_{12}$ is a superconductor with a transition temperature $T_c = 4.1$ K and exhibits normal metallic conductivity with a residual resistance ratio of about 90.^(3,4,5) Metallic conductivity is also observed for $PrFe_4P_{12}$ ⁽⁵⁾ and $NdFe_4P_{12}$ ⁽⁶⁾ which undergo magnetic transitions at low temperatures.⁽³⁾ Mossbauer experiments⁽⁷⁾ and magnetic susceptibility measurements⁽⁴⁾ on $LaFe_4P_{12}$ are consistent with completely demagnetized iron in these compounds, suggesting that the properties of members of the series are determined by the M constituent. In this paper we report the preparation of UFe_4P_{12} for the first time, and report measurements of the electrical resistivity and magnetic susceptibility of both UFe_4P_{12} and $CeFe_4P_{12}$. Our results imply that delocalized f-electrons are present in these two compounds and are strongly hybridized with electrons of the surrounding iron-phosphorous sublattice. This leads to a significant departure of their electronic properties from those expected based on the other MFe_4P_{12} compounds.

Measurements of UFe_4P_{12} and $CeFe_4P_{12}$ were performed on single crystal specimens that were grown in a molten tin solvent.⁽³⁾ Electrical resistivities were measured using a standard 4-wire technique. The magnetic susceptibility of $CeFe_4P_{12}$ was measured with a Faraday magnetometer⁽⁸⁾ in 8531 gauss applied magnetic fields and of UFe_4P_{12} with a SQUID magnetometer in 10 kgauss. The body-centered

cubic crystal structure⁽¹⁾ of $\text{UFe}_4\text{P}_{12}$ and $\text{CeFe}_4\text{P}_{12}$ was verified using x-ray diffraction analysis.

The electrical resistivities of $\text{UFe}_4\text{P}_{12}$ and $\text{CeFe}_4\text{P}_{12}$ are shown in Fig. 1. The curves are normalized to the room temperature values which we estimate to be greater than $1000 \mu\Omega\text{-cm}$, although precise values could not be determined due to the irregular shape of the crystals. For both, the resistivity rise with decreasing temperature by over six orders of magnitude demonstrates clearly that they are semiconductors. To our knowledge this is the first example of an isostructural series of metallic rare earth compounds with the Ce member being non-metallic. Both $\text{UFe}_4\text{P}_{12}$ and $\text{CeFe}_4\text{P}_{12}$ can be fit only over the limited temperature range $85\text{K} < T < 140\text{K}$ to an activated conduction form, $R = R_0 \exp(\Delta E/k_B T)$, where ΔE is the activation energy and k_B is Boltzmann's constant. The values $\Delta E/k_B = 360\text{K}$ and 1500K , respectively, are obtained. Below 85K both curves show a break, or knee, and can no longer be described by simple activated conduction. In the lower temperature, higher resistivity range the measuring current was varied as a check that there was no resistive heating of the samples.

From crystal chemical arguments^(1,9) it was expected that $\text{CeFe}_4\text{P}_{12}$ could be a semiconductor. This was based on the analogy of these phosphides with the semiconducting compound CoP_3 , which is isostructural to the iron phosphorus sublattice in the $\text{MFe}_4\text{P}_{12}$ structure.⁽¹⁰⁾ If Ce were tetravalent, it would contribute the necessary four conduction electrons to the iron-phosphorus sublattice, thus achieving the same electron concentration as CoP_3 . In

$\text{LaFe}_4\text{P}_{12}$, which is a good metal, the rare earth ion is trivalent. If Ce were to be nearly trivalent in the $\text{MFe}_4\text{P}_{12}$ phase, one would expect metallic (or perhaps Kondo-like) conductivity and a strongly temperature dependent susceptibility. The fact that $\text{CeFe}_4\text{P}_{12}$ is a semiconductor and shows very small, nearly temperature independent susceptibility (see below) would indicate a nearly tetravalent state for Ce or perhaps strong 4f electron hybridization. However, this argument is weakened somewhat when a comparison is made with $\text{ThFe}_4\text{P}_{12}$ where Th is almost certainly tetravalent. Our preliminary resistivity measurements show poor metallic conductivity for $\text{ThFe}_4\text{P}_{12}$. In $\text{UFe}_4\text{P}_{12}$ semiconducting behavior is accompanied by localized moment type magnetism. Thus this system may possess two localized 5f electrons, making the U ions in this system analogous to Pr. It seems likely that the itinerant f-electrons present in $\text{UFe}_4\text{P}_{12}$ and $\text{CeFe}_4\text{P}_{12}$ strongly hybridize with the conduction electrons and open a gap in the electronic density of states at the fermi energy. This may be analogous to the hybridization gap seen in the intermediate valent systems SmB_6 and $\text{SmS}^{(11)}$ except that these materials have considerably smaller activation energies than $\text{CeFe}_4\text{P}_{12}$ and $\text{UFe}_4\text{P}_{12}$. Finally, we see that the lattice constants for $\text{UFe}_4\text{P}_{12}$ and $\text{CeFe}_4\text{P}_{12}$ (7.7729 \AA and 7.7920 \AA , respectively) are the smallest known for these types of compounds, and this lends credence to the argument for hybridization.

The magnetic susceptibility of two samples of $\text{CeFe}_4\text{P}_{12}$ are shown in Fig. 2 along with that of $\text{LaFe}_4\text{P}_{12}$ for comparison. The upturns

at low temperature for $\text{CeFe}_4\text{P}_{12}$ can be fit quite well to a Curie law which varies by an order of magnitude between the two batches of $\text{CeFe}_4\text{P}_{12}$ crystals. The temperature independent contribution to the susceptibility of both batches is nearly the same. We therefore attribute the upturns to impurities, which are most likely second phases on the surface of the crystals, although some part of the upturn of the second batch may be intrinsic. The susceptibility of the second batch can be characterized by a temperature independent term $\chi_0 = 2.6 \times 10^{-4} \text{ cm}^3/\text{mole}$ and a Curie term equivalent to 0.3% Ce^{3+} impurity ions per formula unit. Thus the susceptibility of $\text{CeFe}_4\text{P}_{12}$ is roughly a factor of two smaller than that of $\text{LaFe}_4\text{P}_{12}$, and the occurrence of a Ce compound having a much smaller susceptibility than the isostructural La compound is a rather unusual result.

The magnetic behavior of $\text{UFe}_4\text{P}_{12}$ as seen from Fig. 3 is very different from that of $\text{CeFe}_4\text{P}_{12}$. A ferromagnetic-like transition at 3.15 K was inferred from ac susceptibility measurements of $\text{UFe}_4\text{P}_{12}$. In addition, the magnetization in fields up to 3 T showed strong field dependence and attained $1.2 \mu_B/\text{U-atom}$ at $T=1.9$ K. Magnetic hysteresis was detected for temperatures below the Curie temperature. The small positive Curie-Weiss temperature in Fig. 3 is consistent with low temperature ferromagnetic order. We note that the ferromagnetic order cannot be mediated by conduction electrons, as $\text{UFe}_4\text{P}_{12}$ is a semiconductor. The inverse susceptibility vs temperature data of Fig. 3 deviate somewhat from a Curie-Weiss law at high temperature and give an effective moment of $2.25 \mu_B/\text{U-atom}$ at low temperatures. This moment

could be accounted for by a $5f^2$ configuration reduced by crystalline electric field effects or hybridization.

In summary, the properties of the compound UFe_4P_{12} are reported for the first time. Our results presented above on the resistivity and magnetic susceptibility of $CeFe_4P_{12}$ and UFe_4P_{12} are highly unusual in comparison to the other isostructural members of this class of compounds. Strong hybridization of the f-electrons of the Ce and U atoms with the conduction electrons is likely to be responsible for this unusual behavior.

We thank Z. Fisk and A. L. Giorgi for many informative discussions, and R. B. Roof for performing the x-ray diffraction analysis of the UFe_4P_{12} sample. This work was performed under the auspices of the US Department of Energy (LANL and UCSD) and supported by the US Department of Energy under Grant No. DE-AT03-76ER-70227 (UCSD) and the National Science Foundation under Grant No. 82-03690 (Tufts).

REFERENCES:

- a. Permanent address: General Motors Research Laboratory, Warren, MI.
1. W. Jeitschko and D. J. Braun, Acta Crystallog. B33, 3401 (1977).
2. D. J. Braun and W. Jeitschko, J. Less-Common Met. 76, 33 (1980).
3. G. P. Meisner, Physica 108B, 763 (1981).
4. G. P. Meisner, G. R. Stewart, M. S. Torikachvili and M. B. Maple, in Proc. LT-17, ed. by U. Eckern, A. Schmid, W. Weber and W. Wuhl, Elsevier, 1984, 711.
5. M. S. Torikachvili, M. B. Maple and G. P. Meisner, in Ref. 4, 857.
6. M. S. Torikachvili, M. B. Maple and G. P. Meisner (unpublished).
7. G. K. Shenoy, D. R. Noakes and G. P. Meisner, J. Appl. Phys. 53, 2628 (1982).
8. D. K. Wohlleben and M. B. Maple, Rev. Sci. Instr. 43, 1573 (1971).
9. G. P. Meisner, PhD Thesis, University of California, San Diego, 1982.
10. J. Ackerman and A. Wold, J. Phys. Chem. Solids 38, 1013 (1977).
11. For a review see Valence Fluctuations in Solids, ed. by L. M. Falikov, W. Hanke and M. B. Maple, North-Holland, Amsterdam, 1981.

FIGURE CAPTIONS:

- Fig. 1: The electrical resistances, R , of $\text{UFe}_4\text{P}_{12}$ and $\text{CeFe}_4\text{P}_{12}$ normalized to the room temperature resistance R_{RT} .
- Fig. 2: The magnetic susceptibility of $\text{CeFe}_4\text{P}_{12}$ for two batches of crystals. The susceptibility of $\text{LaFe}_4\text{P}_{12}$ is shown for comparison.
- Fig. 3: The inverse magnetic susceptibility of $\text{UFe}_4\text{P}_{12}$. The solid line represents an effective moment of $2.25 \mu_B/\text{U-atom}$.

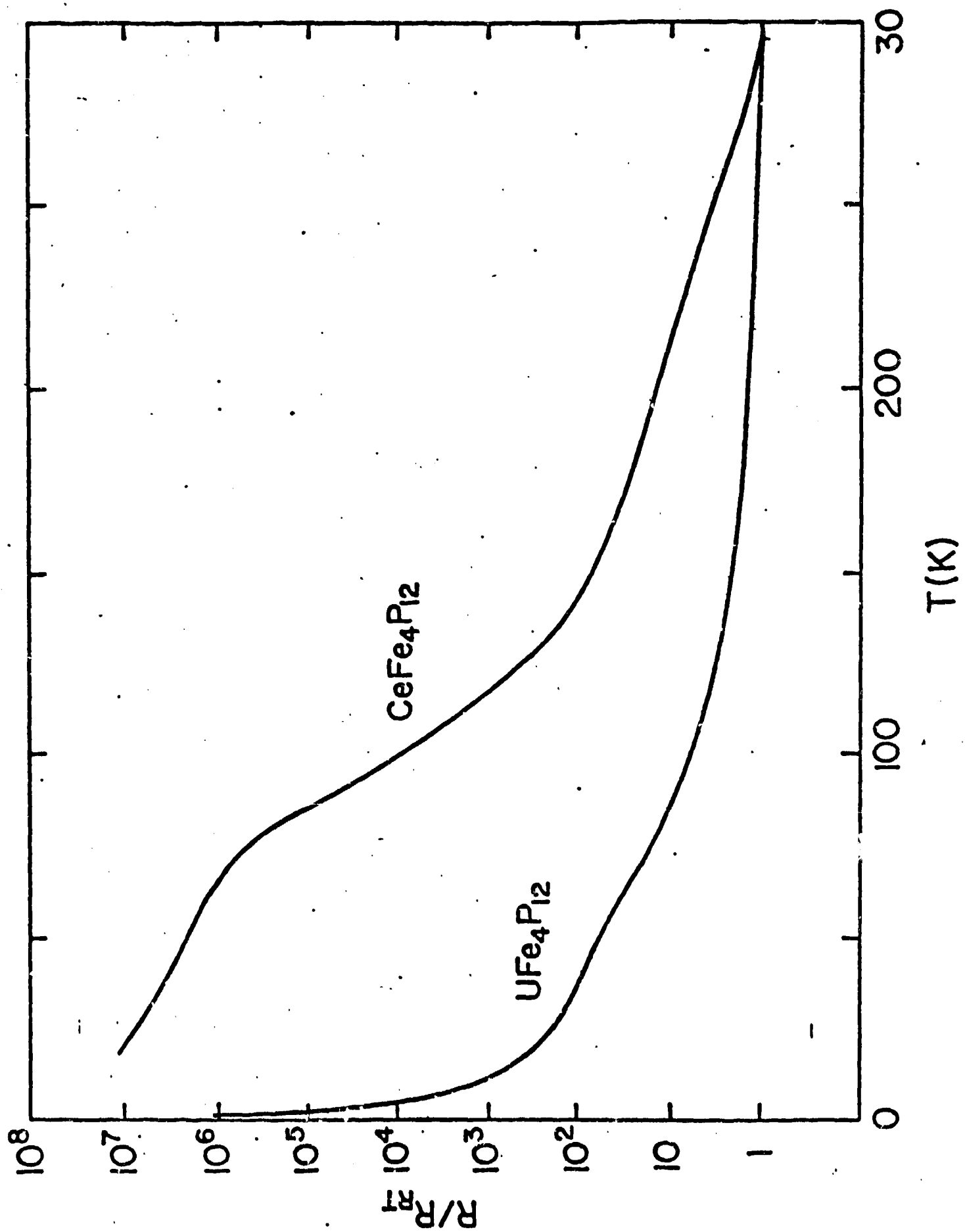


Figure 1

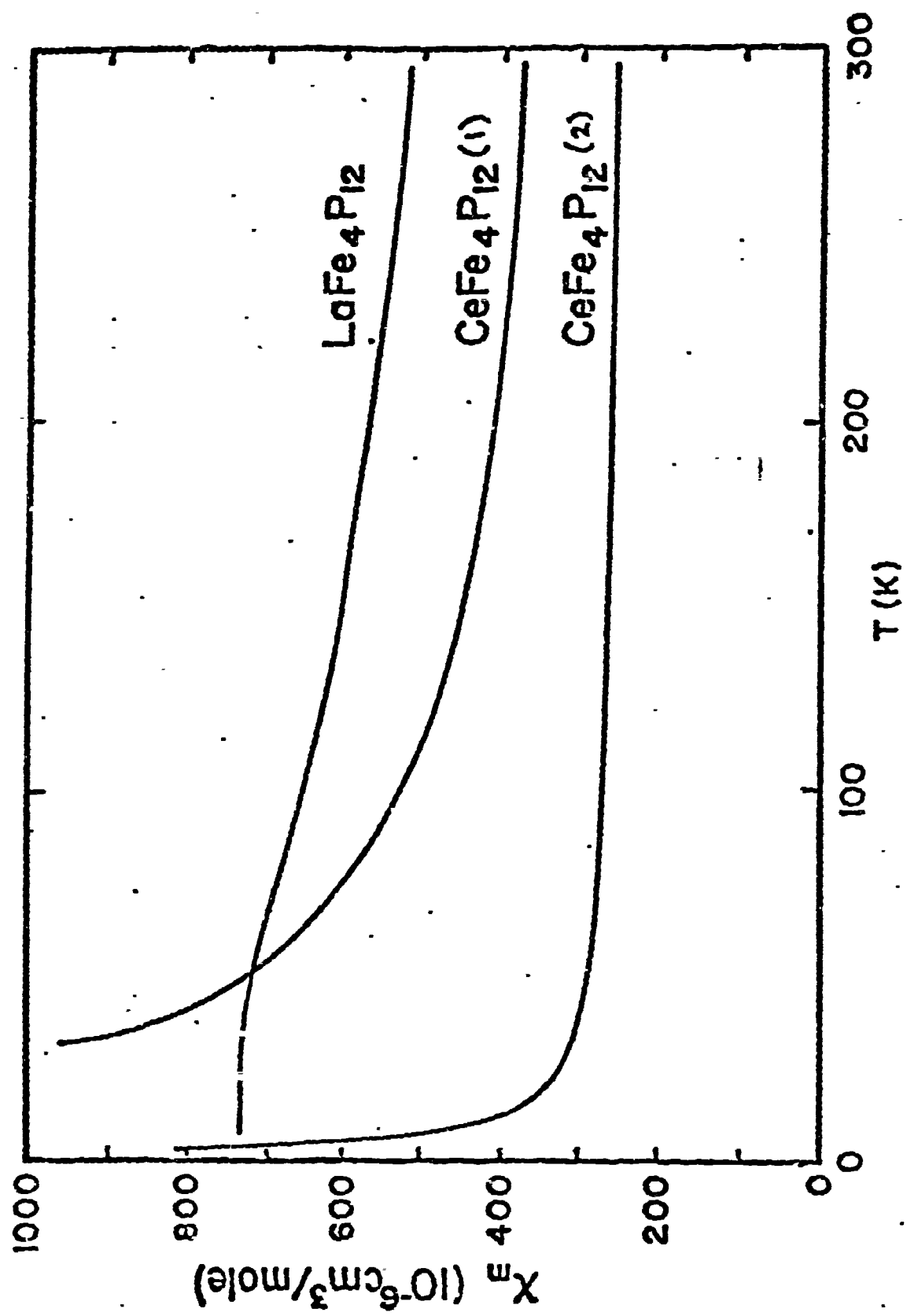


Figure 2

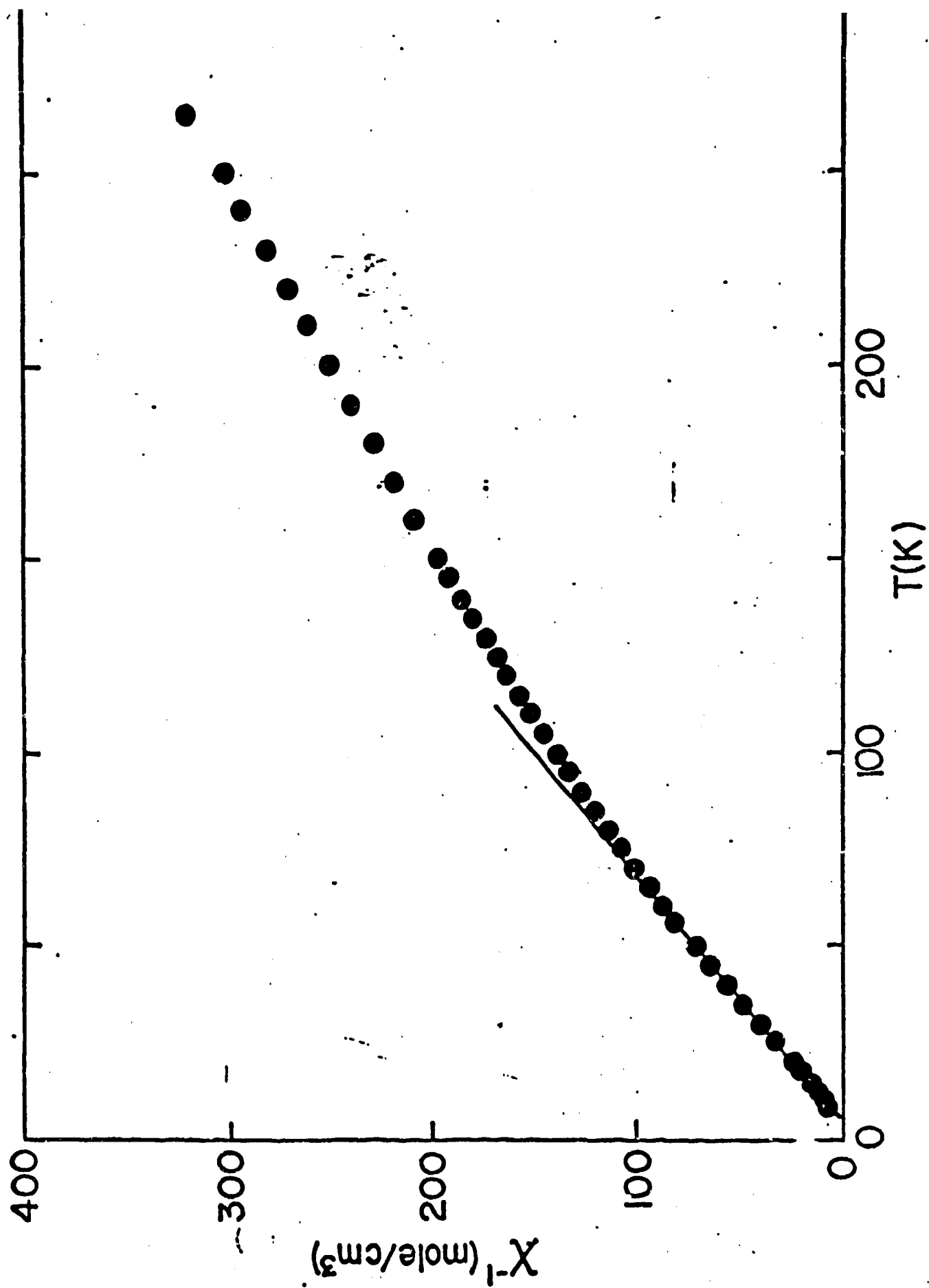


Figure 3